

Influence of Diluent Type on Palladium Extraction from Aqueous Solutions Using DC18-Crown-6

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Abstract

In this paper, extraction of palladium from chloride media by DC18-Crown-6 (dicyclohexyl-18-crown-6 ether) as effective extractant and MIPS and chloroform as diluent has been investigated. The extraction parameters including pH, carrier and feed concentration, and contact time were studied in detail. The results indicated that the efficiency of palladium extraction by DC18-Crown-6 is not very high. Potassium chloride (KCl) was added to the feed solution to form a stable complex with the crown ether. In the presence of KCl, the extraction efficiency could be improved. Generally, the results revealed that chloroform is more suitable than MIPS for this extraction system. At the same conditions, palladium could be separated about 65% with chloroform after 10 minutes, while only 22% was extracted with MIPS after 180 minutes.

Keywords

Solvent Extraction; Palladium; Dicyclohexyl-18-Crown-6; Chloroform; MIPS

Introduction

Nowadays, pollution by heavy metals is a major environmental problem for different countries. One of these metals is palladium which is very worthy (693 \$/oz, December 2012) and has wide applications as catalyst in oil refineries and petrochemical plants, jewelry, electrical and surgery equipments. This metal exists in liquid streams because of industrial effluents and wastewaters discharging. The maximum content of palladium in drinking water can be 0.03 µg/day (for each person) (Kielhorn, 2002). In the last decade, the sources of palladium have been decreased, which is in contrast to its increment consumption in various industries (Table 1 and Table 2). Extraction of palladium from wastes is so important because all palladium compounds are toxic and cancerous, but its price is high.

For palladium recovery from acidic media, hydrometallurgical methods are preferred compared to pyrometallurgical methods because of lower energy consumption. Among the hydrometallurgical methods, solvent extraction is the most applied and classic method. In this process, the organic and aqueous phases are kept in contact and metal ions are transferred from aqueous to organic phase. Some parameters such as pH, feed concentration, extractant concentration, and contact time affect the extraction efficiency (Zakir Hossain, 2000; Kargari, 2006).

Many solvents have been used for palladium extraction until now (Table 3). In recent years, special kinds of macrocyclic extractants known as "Crown ethers" having attracted more attention in the field of metal ions separation, are organic molecules with one or more cycle in their structures and also non uniform atoms with the ability of forming internal holes enriched by electrons, characterized with higher selectivity and extraction rate in comparison with common extractants for Pd²⁺ (Kislik, 2010).

In this work, DC18-Crown-6 (dicyclohexyl-18-crown-6 ether), shown in Fig. 1, has been used as extractant. The effects of parameters including pH, feed concentration, extractant concentration, and contact time on the extraction percent have been investigated. Finally, a comparison between MIPS and chloroform as diluent has been done

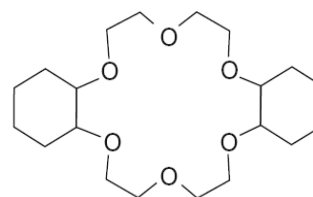


FIG. 1 DC18-CROWN-6 STRUCTURE.

TABLE 1 PALLADIUM SUPPLY: 2000-2011 (MATTHEY, 2011)

Country	Supply (ton)											
	Year											
	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
South Africa	1860	2010	2160	2320	2480	2605	2775	2765	2430	2530	2530	2635
Russia	5200	4340	1930	2950	4800	4620	3920	4540	3660	3560	2850	2850
North America	635	850	990	935	1035	910	985	990	910	750	665	865
Other	105	120	170	245	265	270	270	285	310	335	1360	645
Total	7800	7320	5250	6450	8580	8405	7950	8580	7310	7175	7405	6995

TABLE 2 PALLADIUM DEMAND: 2000-2011 (MATTHEY, 2011)

Application	Demand (ton)											
	Year											
	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Autocatalyst	5640	5090	3050	3450	3790	3865	4015	4545	4460	3895	5200	5510
Recovery	230	280	370	410	530	625	805	1015	1115	950	1370	1530
Chemical	255	250	255	265	310	415	440	375	355	345	855	620
Dental	820	725	785	825	850	815	620	630	625	605	760	780
Electronics	2160	670	760	900	920	970	1205	1240	1100	1000	1815	1320
Jewellery	255	240	270	260	930	1430	995	715	855	920	1150	1200
Investment	0	0	0	30	200	220	50	260	420	635	800	830
Other	60	65	90	110	90	265	85	85	75	70	200	200
Total	8960	6760	4840	5430	7355	7355	6605	6835	6775	6520	9410	8930

TABLE 3 PALLADIUM EXTRACTION WITH DIFFERENT EXTRACTANTS

Extractant	Diluent	Feed phase	[HCl]	T (°C)	t (min)	Stripping phase	E (%)	Ref.
DC18C6	Chloroform	HCl	1 M	25	4	Ammonia	~ 100	(Zakir Hossain, 2000)
LIX 84I	Dodecane	HCl	0.1 M	30	120	HCl	97	(Rane, 2006)
Cyanamides	Toluene	HCl	0.01 M	25	1440	-	98	(Mowafy, 2007)
Ketones	Nitrobenzene	HNO ₃	2 M	25	120	Thiourea	99	(Trong, 2007)
Alamine-300	Kerosene	HCl	0.5 M	25	30	Sodium thiosulfate	99.9	(Swain, 2010)
Alamine336	Toluene	HCl	1 M	25	30	Thiourea, HCl	>99	(Sun, 2011)
Cyanex 471X	Kerosene	HNO ₃	2 M	25	10	Thiosulfate	93	(Ahmed, 2011)
Cyphos®IL104	Toluene	HCl	0.1 M	20	20	NH ₄ OH	96	(Cieszyńska, 2012)

Experimental

Reagents and Solutions

A jewellery grade palladium bar with purity of 99.9 % purchased from local market, was foiled and used for stock solution preparation. A stock solution of 0.01M palladium(II) chloride was prepared by dissolving the foiled palladium in 1M HCl. Working solutions for each solvent extraction were prepared by diluting the stock solution to the desired concentrations. Deionized water was used for dilution and preparation of solutions. MIPS, a rich paraffinic liquid solvent, along with chloroform was supplied from Maroon petrochemical Co. and Dr. Mojallali chemicals Co.,

respectively. The typical chemical analysis of the solvent has been presented in Table 4. Potassium chloride, sodium hydroxide, nitric acid, hydrochloric acid, and DC18-Crown-6 which was used without further purification all of reagent grade were supplied from Merck Co. The stock solutions of DC18-Crown-6 organic phase were prepared by diluting DC18-Crown-6 in MIPS and chloroform to a predetermined weight ratio.

Solvent Extraction Procedure

The synthetic aqueous phase (15 ml) containing palladium was equilibrated with an equal volume of DC18-Crown-6 in MIPS or chloroform. After shaking

the mixture for 20 min (chloroform) and 5 h (MIPS) with a Denley shaker, the two phases were separated by centrifugation at 2300 rpm for 5 min. The ratios of the volumes of aqueous to organic phases were kept 1:1. All experiments were carried out at ambient temperature ($25 \pm 2^\circ\text{C}$).

TABLE 4 CHEMICAL ANALYSIS OF MIPS

Parameter	Value	Unit
< n-C10	max 0.5%	wt%
n-C10 to n-C11	min 40%, max 50%	wt%
n-C12 to n-C13	min 43%, max 56%	wt%
> n-C14	max 1.5%	wt%
Aromatic and water	max 100	mg/kg
Total sulfur content	max 1	mg/kg
Kinematic viscosity	1.96×10^{-3} at 20°C	m^2/s
Density	745 at 20°C	kg/m^3

Apparatus

An inductively coupled plasma optical emission spectrometer (ICP-OES), model Varian 735-ES, was used for determination of Pd^{2+} ions in the aqueous solutions. For separation of organic phase from aqueous phase, a Denley centrifuge, model BS400, was used with 6000 rpm maximum speed. A Denley shaker was used for extraction experiments and a precise digital pH meter (Metrohm-780) was used for pH measurement of the aqueous solutions.

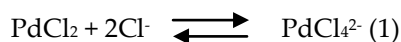
Results and Discussion

Effect of Carrier Concentration

To investigate the effect of carrier concentration on the extraction efficiency, the carrier was used in three concentrations: 0.0005, 0.002 and 0.003 M while other parameters were kept constant. All experimental conditions are given in Table 5.

According to Fig. 2, in the case of MIPS, extraction percent was enhanced with increasing of the ether concentration, but the extraction rate was very low. It was found that DC18C6-mediated palladium transport in this system is negligible due to the relatively high hydration energy of Pd^{2+} ion and its very small size for the cavity of DC18C6. Potassium chloride solution (0.2 M) was added to the feed solution as improver agent. According to reaction (1), in the presence of excess chloride ion, Pd^{2+} exists as a stable low-hydrate complex anion PdCl_4^{2-} and hence, it can easily

accompany the stable $\text{K}^+\text{-DC18C6}$ cation into the organic phase (Jabbari, 1999).



By KCl addition, a red precipitate was observed at the interface of organic and aqueous phases. By replacing chloroform as diluent, the extraction was improved without producing any precipitate. The carrier concentration was considered equal to 0.001 M in the next experiments.

TABLE 5 EXPERIMENTAL CONDITIONS

[KCl] (M)	C_f (ppm)	pH	Speed (rpm)	t_c (min)
0.2	100	2	2300	5

Effect of pH

As it was mentioned that KCl forms a precipitate by using MIPS as diluent but it makes a stable complex with DC18-crown-6 in the presence of chloroform. The effect of pH of the feed solution on the extraction was investigated. The experiments were done in high acidic pH ranges (1, 2, 3, 4, 5) because the palladium hydroxide precipitates at higher pH. The other conditions are according to the Table 5. Based on Fig. 3, in the case of MIPS, the extraction percentage is negligible at any value of pH. While it increases with decreasing of pH in the presence of chloroform, however the extraction percent is low and the maximum value is 25% at $\text{pH}=1$.

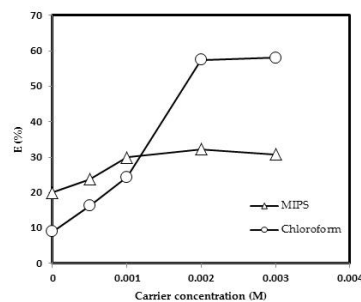


FIG. 2 EFFECT OF CARRIER CONCENTRATION ON THE EXTRACTION PERCENT

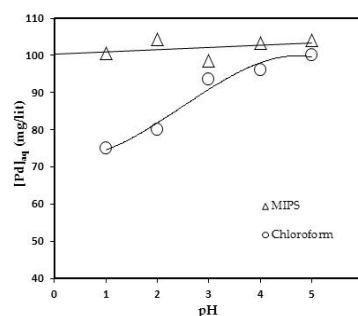


FIG. 3 EFFECT OF FEED PH ON PALLADIUM CONCENTRATION IN THE AQUEOUS PHASE

Effect of contact time

Extraction percent was studied in different contact time (10, 20, 30, 40, 50, and 180 minutes) when the other parameters were constant (Table 5). In the case of MIPS, results revealed that extraction efficiency is enhanced by increasing the contact time of the phases and the maximum percent is 25%. Contrary to expectation, the extraction efficiency is decreased during the time in the presence of chloroform and the most value (65%) is achieved after 10 minutes (Fig. 4). This result shows that $[K^+-DC18C6]_2-[PdCl_4]^{2-}$ complex is rapidly formed according to reaction (2) but it begins to decompose after 10 minutes and some of transported palladium returns to the feed solution.

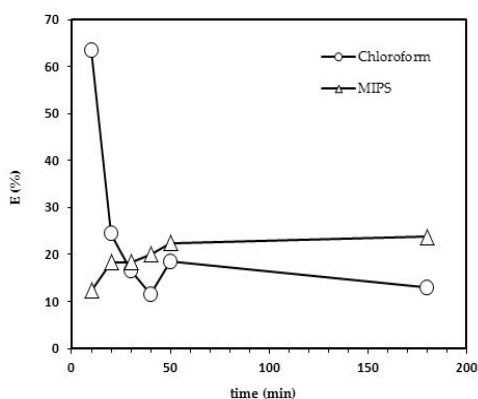
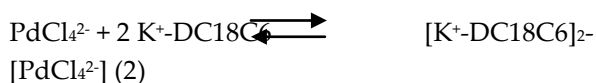


FIG. 4 EFFECT OF CONTACT TIME ON THE EXTRACTION PERCENT

Effect of feed concentration

To evaluate the effect of feed concentration, experiments were performed at different feed concentrations of 20, 50, 200, 500 and 1000 ppm. In all

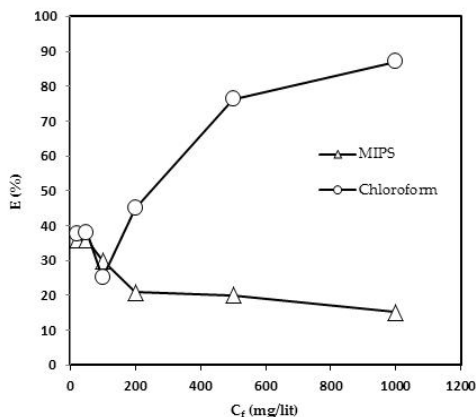


FIG. 5 EFFECT OF FEED CONCENTRATION ON THE EXTRACTION PERCENT

cases, pH value was adjusted at 1 and the other parameters were similar to those given in Table 5. As it was expected that in the case of MIPS, the extraction percent decreased with increment of the aqueous phase concentration (Fig. 5). In the chloroform extraction system, because of the constant concentration of 0.2 M KCl and 0.001 M carrier, the number of formed complexes and subsequently the extraction percent is enhanced with the rise of the feed concentration (reaction 2).

Conclusion

Separation of palladium is very important from economic and environmental points of view. In this work, palladium extraction was performed by DC18-Crown-6 dissolved in MIPS as well as in chloroform. The effects of parameters such as pH, feed concentration, organic phase concentration and contact time on the extraction percent were studied. In the case of MIPS, the extraction percent was negligible by pH variation. An appropriate cation was needed to form a stable complex with the ether. A red precipitate appeared at the interface of organic-aqueous phase when potassium chloride was added as improver agent. By replacement of chloroform as diluent, the extraction efficiency was improved and the maximum value was obtained as 25% at pH=1. The results showed that in both systems, extraction percent was enhanced by increasing the carrier concentration, and that chloroform was better than MIPS. The content of transported palladium with chloroform and MIPS was 65% after 20 min and 25% after 180 min, respectively. In the case of MIPS, the extraction efficiency was declined by increasing the feed concentration, while it ascended by using chloroform due to a restrictive reaction. From these results, it can be concluded that in this system, chloroform as an organic solvent is more effective than MIPS.

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NOMENCLATURE

E Extraction efficiency (%)

t Contact time (min)

T Temperature (°C)

C_F Feed concentration (ppm)

T_c Centrifugation time (min)

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